CEMENT AND LIME MANUFACTURE

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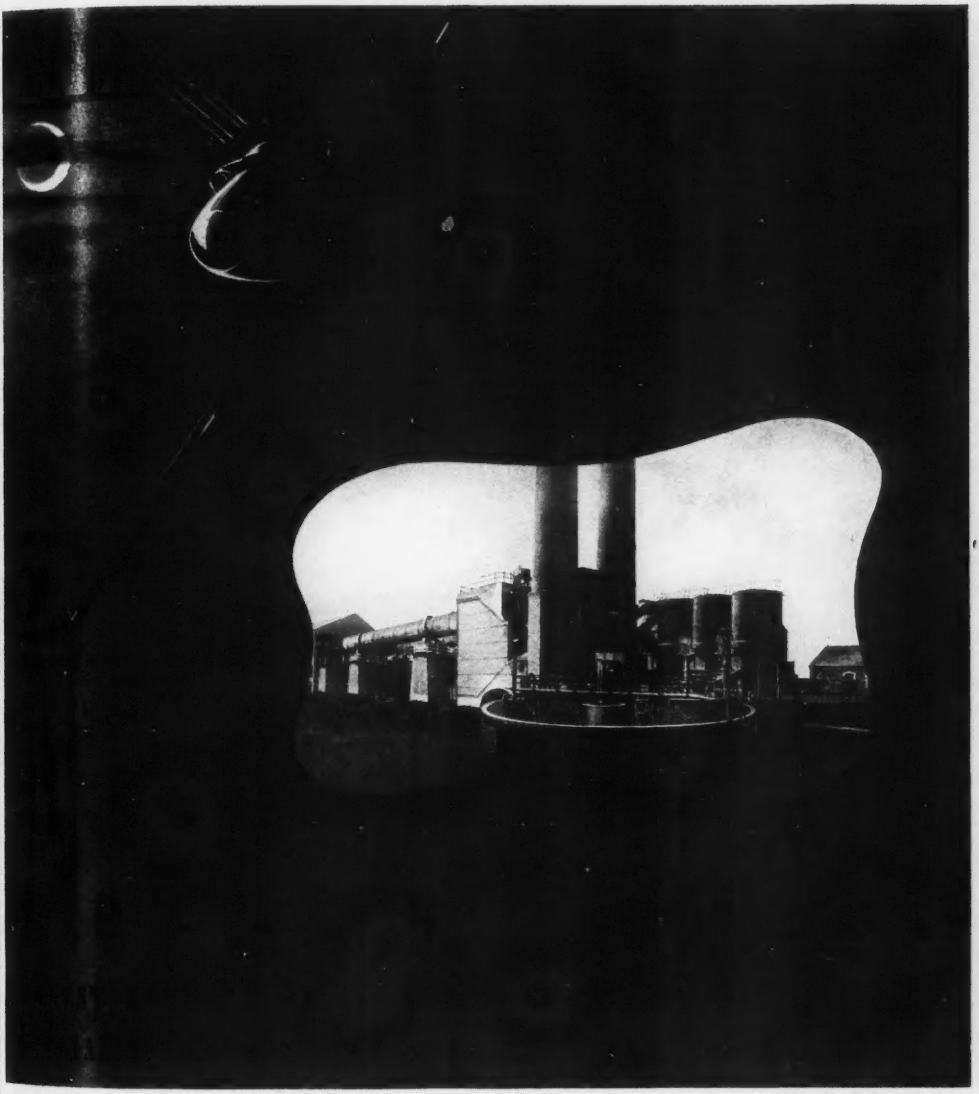

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Selective Crushing of Stone.

IN the following, types of crushers and the characteristics of their products are discussed in a general way. The stone under consideration may be limestone or other hard type as used in the manufacture of cement, for concrete aggregates, and road stone. It will be assumed that the stone has been blasted, quarried, and excavator-handled in the usual way, that the largest occasional pieces will have a cubical content of, say, 12 ft. to 15 ft. (0·75 to 1 ton in weight), and that this size will be handled conveniently by the primary crusher and be easily within that machine's capacity. It is also assumed that the whole of the stone dealt with will be usable or marketable unless defects in the stone are discovered during the crushing process.

A typical classification of the stone delivered to the crushers is indicated by curve A in *Fig.* 1, and the desired classification of the product of the plant (which is purely arbitrary and has not been drawn up with any specific object in view) is as follows:

Through 6 in. sieve	and retained on	4 in. sieve	..	5	per cent.
,,	4 ,,	,,	,,	,,	,,	2½ ,,	,,	..	10	,,	,,
,,	2½ ,,	,,	,,	,,	,,	1 ,,	,,	..	15	,,	,,
,,	1 ,,	,,	,,	,,	,,	½ ,,	,,	..	15	,,	,,
,,	½ ,,	,,	,,	,,	,,	¼ ,,	,,	..	20	,,	,,
,,	¼ ,,	,,	,,	,,	,,	⅛ ,,	,,	..	20	,,	,,
,,	⅛ ,,	,,	..	..	..	..	..	..	15	,,	,,

The stone in the various gradings would be as clean as practicable. As each stage of crushing tends to the production of "fines," the deliberate production of fines in the early stage of crushing is to be avoided as much as possible; this, however, presupposes that it will be possible to produce an additional

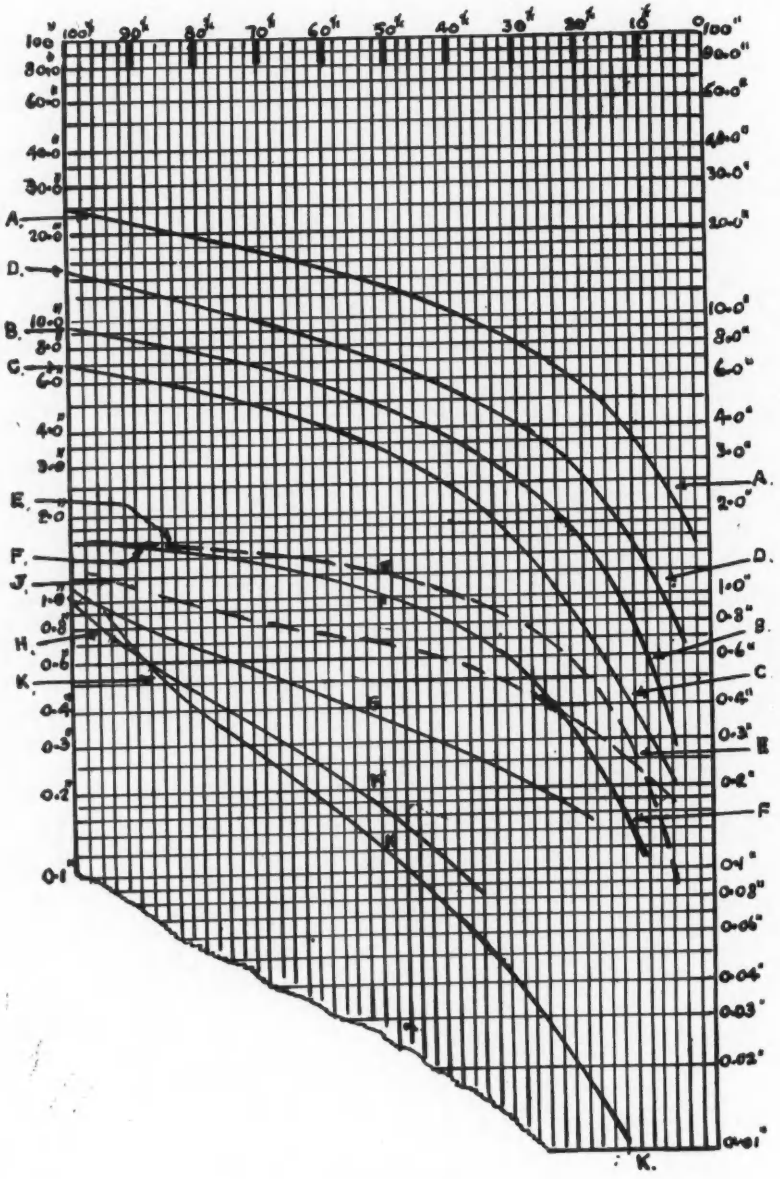
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0
100"
90·0"
80·0"
60·0"
48·0"
40·0"
30·0"
20·0"
10·0"
8·0"
6·0"
4·0"
3·0"
2·0"
1·0"
0·8"
0·6"
0·4"
0·3"
0·2"
0·1"
0·08"
0·06"
0·04"
0·03"
0·02"
0·01"
A.
B.
C.
D.
E.
F.
H.
J.
K.

Fig. 1.

quantity of " smalls " or fines at the finish of the process if it is necessary to do so.

The total product of the plant may be assumed to be 3,000 tons per week (a gross working period of 48 hours), or, say, 75 tons per hour as a net working figure equivalent to a net crushing time of 40 hours per week at full output.

Types of Crushers for Different Purposes.

In considering the classification of the stone at the various stages of crushing, it is necessary to consider the type of crushers that will best meet the conditions, and more especially the types of product that the various crushers are likely to yield.

As pieces of stone up to 12 to 15 cu. ft. are likely to be dealt with, the primary machine should be of the sledging-jaw type, and in order to maintain a large output it will be necessary to accept a relatively large-size product from this machine. At this stage it appears best to visualise a product of, say, 6 in. to 7 in.; facilities must, however, be provided for closing the jaws to obtain a smaller product if necessary. The feed opening of this machine should be large enough to permit the largest pieces of stone to enter easily and to fall at once a distance of 25 per cent. to 30 per cent. of the vertical height of the opening, where useful movement of the jaw takes place.

The classification of the run-of-quarry stone as fed into the primary crusher may be assumed to be generally as indicated by curve A, which is based on a similar feed where the stone was obtained by blasting, handled by excavator, and delivered to the crusher-hopper in four-ton to six-ton batches. This stone was medium hard. The classification was very coarse with the largest pieces up to 24 in. cube; 50 per cent. of the total quantity was greater than the 13 in. dimension; and the amount of small stone was very limited. Curve B shows the classification of the product from this machine with a jaw setting of $6\frac{7}{8}$ in. to $8\frac{3}{4}$ in. This size, however, appears large for the present purpose, and assuming the jaw opening to be reduced to, say, 6 in. to 7 in. or thereabouts, we should obtain a classification in agreement with that indicated by curve C.

It appears best now to review the characteristics of the various types of crushers so as to obtain clear ideas of the duty and the product for which each machine is best suited.

On economic grounds the primary machine cannot be other than of the sledging-jaw type. A gyratory or a single-roll machine would effect the crushing; the former, however, would have to be large and probably costly, while the latter would also be costly and the maintenance cost would be high. There is thus no satisfactory alternative to the jaw-type machine; the quantity capacity of the machine will be very large, but there is no help for this.

For intermediate general duty, if such is required, the single-pair roll machine would serve the purpose. A jaw machine, smaller than that allocated for the primary duty, would also meet the conditions. If a " gravel " type product

is required, a pair-roll crusher, or a cone crusher, would serve the purpose. If smalls, fines, or chippings are required, the hammer-mill cannot be improved upon.

Referring to *Fig.* 1 and comparing curves A, B, and C, it will be noted that curve A for feed and curve B for product, each obtained from the same machine, are very similar in form although there is considerable difference in the size of the material, the latter being obviously much smaller. (This similarity of form is a characteristic of both the jaw and the gyratory crusher, that is to say, the product of both machines is very similar to that of the feed.) If the jaw crusher were closed the characteristic curve would be lowered to, say, C; if the jaws were opened, the characteristic curve would be near to D. Any closing of the jaws, however, would have to be carried out with care owing to the possibility of choking the machine resulting in damage or breakdown. To summarise, any jaw or gyratory crusher fed with stone as at curve A would give a product similar to that of curves B, C, or D—not perhaps exactly the same, but very similar. A different class of stone would not make much difference; in any case it would be sufficiently near for the present purpose.

The characteristic indicated in curve E was obtained from a single-pair roll crusher set to 1⅛ in. to 1¼ in. This machine was fed with the product of a jaw crusher set to 4 in. to 4½ in.; the curve for the roll-crusher feed would therefore be in substantial agreement with that of curve C, although the stone would be rather smaller.

Upon examining curve E, it will be noted that the single-pair roll crusher produces only a limited amount of smalls or fines. This is characteristic of the roll machine, which simply breaks down the oversize pieces, or those pieces that are larger than the space between the rolls, and thus normally produces gravel and not smalls. If the machine were run with "choke" feed it would reduce the stone below the size of its setting; the classification, however, would be substantially the same, though the size of the stone would be generally smaller.

Curve F was obtained from a large cone crusher operating with controlled feed obtained from a large jaw crusher having a setting of about 6 in.; it would thus follow the characteristic of curve B. Curve F indicates the production of the maximum amount of large pieces of stone; in this machine also the amount of smalls is limited; this curve follows very closely curve E for the single-pair roll crusher, but with a slight difference in the smaller sizes.

Curve G was also obtained from a cone crusher, but a smaller size machine. This machine was of the short-head type, of the 4-ft. size, and with 1 in. to 1⅛ in. setting. It was dealing with clean hard stone of from 6 in. to 8 in. cube with only a very small amount of smalls. At the time the figures were obtained the machine was working at about 115 per cent. of its rated capacity, and this accounts for the straight-line characteristic and the small size of its product; the stone was actually being compressed in the feed opening and crushing was being effected by squeezing as well as by the crushing action of the machine.

It need hardly be pointed out that serious risk of breakdown was being run by operating the machine in this way.

A similar curve (J) is taken from the same machine under 85 per cent. controlled-feed conditions, with 1 in. setting as the basic dimension. The characteristic in this case is similar to curve G for the single-pair roll crusher. It is not greatly dissimilar from curve F for the large cone crusher, but there appears to be a reduced quantity of smalls and fines.

The other two curves were obtained from the product of hammer-mill machines, curve H from a machine dealing with 75 to 80 tons of stone per hour, and curve K from a machine dealing with 250 to 300 tons per hour. These hammer mills are both of the Pennsylvania Co.'s make. The smaller machine (curve H) had been in quarry service for ten or twelve years under industrial conditions, dealing with run-of-quarry stone up to 6 in. or 7 in. The larger machine (curve K) was nearly new when the figures were obtained; its feed was the product of a large gyratory machine, with a 9 in. setting, mixed with fines, and may be regarded as run-of-quarry stone of up to 9 in. The rotor of this machine is reversible and it is the rule to change the direction of rotation every few days and so secure equal wear on both sides of the hammers. The operation of this large hammer-mill is described fully in *Rock Products* for February 1939, where it is stated that the wear on the hammers amounted to only 3 lb. weight for every 1,000 tons of stone crushed.

If the crusher products now under consideration were required for mill feed, there would be no satisfactory alternative to the hammer machine for the final reduction owing to the large amount of smalls and fines that are normally produced.

Consideration of the information shown on—or deducible from—*Fig.* 1 may now take the following lines.

Curve C indicates that a single pass through a sledging-jaw crusher with a 6-in. setting will produce the following approximate quantities of graded stone:

		+ 6 in.	..	10 per cent., say	$7\frac{1}{2}$ tons
(*a*)	— 6 in. ..	+ 4 ,,	..	28 ,, ,, ,,	21 ,,
(*b*)	— 4 ,, ..	+ $2\frac{1}{4}$,,	..	24 ,, ,, ,,	18 ,,
(*c*)	— $2\frac{1}{4}$,, ..	+ 1 ,,	..	14 ,, ,, ,,	$10\frac{1}{2}$,,
(*d*)	— 1 ,, ..	+ $\frac{1}{2}$,,	..	9 ,, ,, ,,	7 ,,
	— $\frac{1}{2}$,, ..		..	15 ,, ,, ,,	11 ,,

It will be noted that about 10 per cent. of the product is above the 6 in. (setting) dimension. This is quite usual and can easily be corrected for by setting the machine a little closer; this change of setting can easily be done and may have frequently to be carried out under normal operating conditions. Excess quantities are indicated at (*a*) and (*b*); this is all to the good as any excess can be passed on to the machines producing the smalls and fines. A slight shortage exists at (*c*), but this may be ignored as it may be rectified with the larger quantity.

Screens.

A sieve or screen will clearly be necessary to obtain classification, and the type or form of sieve should now be briefly considered so that correct arrangements may be made at the finishing end of the crushing process. A rotating screen of heavy construction may be considered satisfactory for dealing with this very coarse and cutting material, especially as the quantity is small. This screen should be designed for dealing with the four grades indicated at (*a*), (*b*), (*c*), and (*d*); there should be no difficulty here, though good design is essential.

Having dealt with the primary crushing and classification down to the 1-in. stage, it has become clear that no intermediate crushing will be required providing the hammer mill be adopted as the final crushing unit and that this mill will lend itself to the production of a range of size of product. This hammer mill should be fitted with a lower grating of rather open mesh or wide spaces so that the crushed stone has a free discharge. The level of this grating should be adjustable so that it can be brought closer to, or moved farther from, the hammer radius; this arrangement should provide reasonable control over the size of product. It may prove necessary to provide a very free discharge in order to obtain a still larger product and to resort to closed-circuit crushing to obtain additional fines under the altered conditions; this can only be determined when the plant is in operation, and is worth a little trouble if it proves possible to avoid intermediate crushing.

A good type screen will also be required for dealing with the product of the hammer crusher. This screen will require spaces or openings of $\frac{1}{2}$ in., $\frac{1}{4}$ in., and $\frac{1}{8}$ in. The screen should preferably be of the vibrating-mechanical type, of good construction, and having good facilities for changing and replacing the screen sheets.

It is felt that the foregoing will enable a plant to be designed when the class of stone and the classification of the final product are known. The outline has been fully worked out, and there should be no difficulty in finishing the design to known requirements.

Removal of Fire Rings in Rotary Kilns.

A NEW method of removing fire rings in rotary kilns is described in a recent number of *Pit and Quarry*. It is claimed for this process that (*a*) the entire procedure does not require over 15 minutes; (*b*) the slag is broken into large pieces, making removal simple; (*c*) serious contamination of the product is avoided; (*d*) a complete shut-down for slag removal is eliminated; (*e*) damage to the refractory lining is avoided; (*f*) it is safe; (*g*) great saving in operating time is effected; (*h*) low cost.

The procedure is as follows: (1) Determine where the slag forms. Provide for a considerable length of operation, as fire rings move up and down the kiln

Fig. 1.—Preparing Small Opening in the Fire Ring to allow release of Gas above inner face of Kiln Lining.

according to changing conditions. (2) Cut with a torch a number of round openings through the shell of the kiln (*Fig.* 1). Each opening should be ground to a true circle to reduce the possibility of tearing the shell plate. (3) Twelve-inch diameter plates, formed to the curvature of the kiln shell, are welded about each opening for purpose of reinforcement (*Fig.* 2). (4) Three-inch pipe sleeves with plugs for closures are firmly welded over each opening (see 5, *Fig.* 4). (5) On the inside of the shell ½-in. by 2-in. flat iron is welded on edge at three sides of each opening; this prevents shifting of the bricks (see 6, *Fig.* 4). (6) A small pneumatic chipping hammer is used to dress the radial core out of

two matched rotary-kiln liners (see 7, *Fig.* 4). (7) When slag has formed over the openings to a point where it is ready for removal, a small air-tool should be used to dress out the openings for the cartridges. This is a minute's work. Workmen should wear gloves with cuffs to prevent spalls from hot slag from

Fig. 2.—CO_2 cartridge with Holder in position.

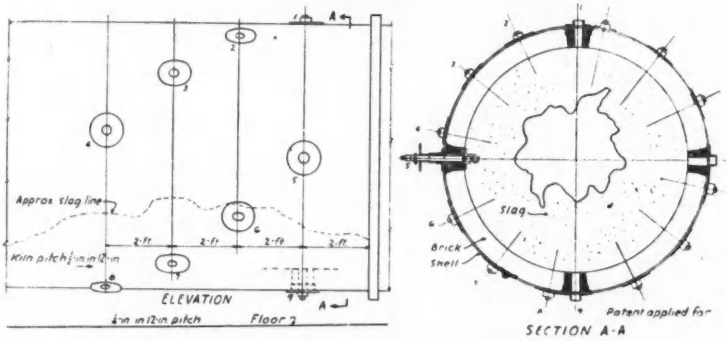

Fig. 3.—Shell Openings to Slag Formation Area.

entering their sleeves (*Fig.* 1). (8) Attach the cartridge holding device to the pipe sleeve (*Fig.* 4). (9) Insert the cartridge to which lead wires have been attached. Follow blasting technique. Have the lead wire detached from the battery. The cartridge is placed so as to give the gas-exit ports about 1-in. clearance above the inner face of the fire-brick lining. Experience will indicate

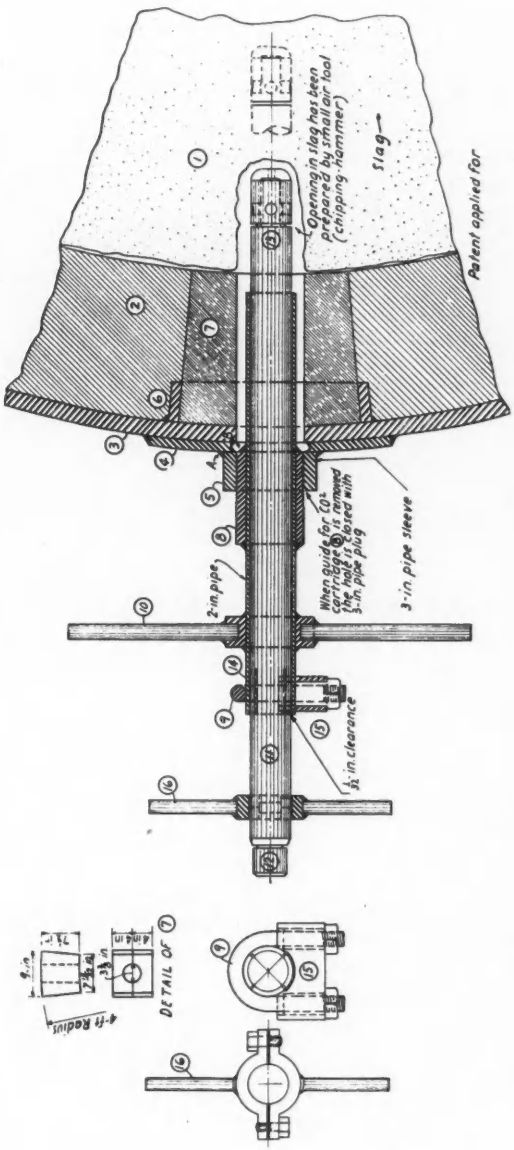
Slag
Opening in slag has been prepared by shaft or tool (chipping hammer)
Patent applied for
When guide for cartridge (9) is removed the hole is closed with 3-in. pipe plug
3-in. pipe sleeve
2-in. pipe
½ in. clearance
DETAIL OF (7)
4-ft Radius

Fig. 4.—Method of Inserting Cartridge. (1) Slag formation; (2) refractory lining; (3) kiln shell; (4) steel plates welded to kiln shell; (5) pipe sleeve; (6) reinforcement welded to inside of shell; (7) refractory liner; (8) cartridge guide; (9) clamp to hold cartridge on release of gas; (10) handle; (11) cartridge; (12) lead wire connection; (13) exit gas ports; (14) contraction slots; (15) clamping device; (16) detachable handle.

the point at which the best results are obtained (*Fig.* 3). (10) Press the battery; the slow expansion of the gas will force the slag loose from the refractory lining in large pieces. (11) Experience will indicate the number of cartridges required for a given condition.

Ordinarily the total kiln shut-down will amount to about ten minutes. The cartridge used is an adaptation of the " Cardox " cartridge, as used in the mining of coal. The energy medium of the " Cardox " cartridge is carbon-dioxide gas. A small chemical heating element in the cartridge may be energised at will to cause expansion of the gas up to the pressure value at which release of the gas from the cartridge occurs. In the application of the " Cardox " device to rotary kilns the released gas penetrates the natural fissures and cleavage lines, separating the slag from the refractory lining, and breaking it into large pieces which may be removed easily.

Potassium Sulphate in Cement Clinker.

AN investigation at the United States Bureau of Standards on the compositions and properties of solutions obtained from cement pastes with and without admixtures is reported by Messrs. G. L. Kalousek, C. H. Jumper and J. J. Tregoning.

It was found that the percentage of the total K_2O and Na_2O which dissolved was varied extensively among the clinkers. In general, the results of chemical analyses of solutions which result from the action of water on a mixture of compounds are not sufficient in themselves for identification of the original compounds. These data, however, were of such a nature as to permit the conclusion that part of the potassium is present in many cement clinkers in a compound not considered previously. Because of this, and of the increasing interest in the alkalis, the results pertaining to K_2O and Na_2O are presented now, and the remainder of the data will be published later.

Twelve commercial Portland cement clinkers consisting of eight of the standard, three of the modified, and one of the sulphate-resistant type were ground to an average fineness[1] of 1800-1900 sq. cm. per gramme. As shown by the analytical results in Table 1, the percentages of K_2O and Na_2O varied through a wide range for these clinkers.

Paste, made by mixing 7000 g. of ground clinker and 245 g. of water for 2½ minutes, was placed in a specially constructed air-pressure filter and the solution removed by the application of compressed air. The filter consisted of heavy brass tubing, 10-in. in diameter, to which was securely attached a baseplate perforated with holes $\frac{1}{16}$-in. in diameter and spaced $\frac{3}{4}$-in. apart. The filtering media, placed in the following order on the perforated base, were first a filter paper, next a No. 150 screen cloth, then another filter paper, and finally a No. 8 screen cloth. The iron cover plate, with accompanying rubber gas-jet and connection to the air line, was fastened to the filter-drum collar with steel stud bolts. Air pressure was applied initially at 25 lb. per square inch and increased

TABLE 1.—PERCENTAGES OF K_2O, Na_2O, AND SO_3 IN CLINKER; GRAMMES PER LITRE OF K_2O, Na_2O, AND SO_3 FOUND IN SOLUTION; AND PERCENTAGES OF TOTAL K_2O AND TOTAL Na_2O THAT ENTERED SOLUTION FROM HYDRATING CLINKER.

No. Clinker		Percentage of clinker		g.K_2O/liter found in solution at:		g.Na_2O/liter found in solution at:		g.SO_3/liter found in solution		Percentage of total K_2O found in solution at:		Percentage of total Na_2O found in solution at:	
1	2	3	4	5	6	7	8	9	10	11	12	13	14
	K_2O	Na_2O	SO_3	7 min.	2 hr.	7 min.	2 hr.	7 min.	2 hr.	7 min.	2 hr.	7 min.	2 hr.
1	0.05	0.56	0.09	0.02	0.09	0.072	0.586	0.002	0.002	1	6	0.4	3.8
2	0.25	0.04	0.00	0.429	0.956	0.133	0.194	0.004	0.006	6	14	12	18
3	0.11	0.02	0.01	0.280	0.309	0.062	0.071	0.004	0.004	9	10	10	12
4	1.32	0.09	0.51	18.65	19.71	0.481	0.790	7.900	3.348	50	52	19	31
5	1.05	0.05	0.37	13.21	15.08	0.106	0.166	2.811	0.134	44	50	8	12
6	0.53	0.62	0.18	5.99	7.22	2.20	3.37	0.804	0.058	40	49	12	19
7	0.18	0.18	0.32	2.84	3.20	1.26	1.57	0.019	0.000	56	62	25	31
8	0.20	0.17	0.30	3.35	3.48	1.47	1.66	0.007	0.005	58	61	30	34
9	0.09	0.87	0.35	0.352	0.352	2.99	3.89	0.000	0.003	14	14	12	16
10	0.26	0.13	0.12	1.45	1.83	0.244	0.344	0.009	0.019	20	25	7	9
11	0.37	0.43	0.12	3.23	3.48	1.79	1.97	0.019	0.010	31	33	15	16
12	0.76	0.12	0.28	10.73	11.66	0.449	0.505	0.024	0.027	49	54	13	15
										15 min.	—	15 min.	—
A	0.58	0.35	0.23							43	—	18	—
B	0.47	0.27	0.17							45[1]	—	20[2]	—
C	0.74	0.51	0.37							70[1]	—	20[2]	—

[1] Estimated. [2] It is assumed that 20 percent of Na_2O dissolved

at the rate of about 12 lb. per square inch per minute to 75 lb. per square inch. The time required for filtering generally varied from two to four minutes. Clear solutions were obtained from all clinker pastes. One paste of each clinker, or clinker plus admixture, was filtered immediately upon completion of mixing with water. The time between the addition of the water until completion of the filtering averaged seven minutes. A second corresponding paste was permitted to stand for 1 hour 55 minutes after completion of mixing and then filtered as the first. The total time of contact of hydrating clinker with water averaged two hours for the second paste.

The solutions were analysed according to accepted analytical methods for all constituents of the clinker. An error of only 0·01 or 0·02 per cent. absolute, in the analytical results, for K_2O, Na_2O, or SO_3 in clinkers which contained these in small amounts, alters markedly the calculated values reported in Tables 1 and 2. Therefore, all precautions were observed and duplicate or triplicate determinations of these constituents were made. Blank determinations were made and appropriate corrections were applied.

Only the salient data pertaining to the alkalis are presented in this paper. In Table 1, columns 2, 3 and 4, are reported the percentages of K_2O, Na_2O, and SO_3 in the clinkers. In columns 5 and 6, and 7 and 8, are given, respectively, the grammes per litre of K_2O and Na_2O that were found in solution at seven minutes and two hours; and columns 9 and 10 show the grammes per litre of SO_3. Columns 11 and 12, and 13 and 14, give the calculated percentages of the total K_2O and Na_2O in the clinkers that dissolved in the two periods.

An examination of the data in columns 11 and 12 shows that 1 to 58 per cent.

TABLE 2.—MOLECULES K_2O FOUND AND MOLECULES SO_3 CALCULATED PER LITRE SOLUTION.

Clinker No.	K_2O in solution at 7 minutes	SO_3 available in clinker
4	0·197	0·182
5	0·140	0·132
6	0·064	0·064
7	0·030	0·114
8	0·036	0·107
11	0·035	0·043
12	0·114	0·100
A	0·089	0·096
B	0·097	0·097
C	0·164	0·136

of the total K_2O present, and from less than 1 per cent. to 30 per cent. of the total Na_2O present, dissolved in seven minutes. The consistently high percentage solution of K_2O from a number of the clinkers permits a division of these results into two groups. Thus, clinkers Nos. 4, 5, 6, 7, 8, and 12 contain readily soluble K_2O, 40 to 58 per cent. of the total amount present going into solution in seven

minutes, and although clinker No. 11 shows only 31 per cent. it is included in this group. The fraction of the total Na_2O that was removed is seen to be generally much lower, varying from 8 to 30 per cent. Clinkers Nos. 1, 2, 3, 9, and 10 of the second group show only a 1 to 20 per cent. solution of K_2O. With the exception of clinker No. 10, in this group the percentages of total Na_2O and K_2O that dissolved are, within limits of experimental error, nearly the same for any given clinker.

An examination of the data shows that the solution of the alkalis between seven minutes and two hours, for both groups of clinkers, is relatively slow, the average increases of K_2O and Na_2O being respectively $4\frac{1}{2}$ and 5 per cent. From the data in Table 1 it is also apparent that the factors governing the solubilities

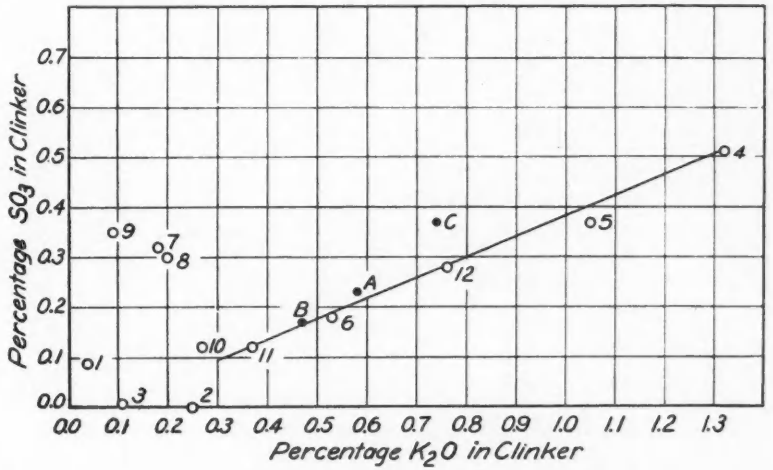

Fig. 1.—Percentage of SO_3 in Clinkers Plotted against Corresponding Percentage of K_2O.

of these two constituents differ among the clinkers, indicating a variation of the manner in which K_2O and Na_2O respectively are combined in the clinkers. No correlation could be found between the amounts of Na_2O or $Na_2O + K_2O$ and SO_3, nor between other constituents in the clinkers or in the solutions. However, as discussed below, five of the seven clinkers which contained the readily soluble K_2O showed a correlation between the SO_3 and K_2O contents.

As shown in *Fig.* 1, wherein are plotted the percentages of SO_3 against the percentages of K_2O in the clinkers, the SO_3 content of the eight clinkers having more than 0·3 per cent. K_2O bears nearly a straight-line relationship to the K_2O content. Three of these points (A, B, and C) are taken from Roller's data.[2] This straight-line relationship, the slope of the curve corresponding to a molar ratio of 2·1 K_2O : 1·0 SO_3, is very striking because five of the six clinkers for which

that data are available contain potash of which about 50 per cent. dissolved in seven minutes. The sixth clinker (No. 11) shows 31 per cent. loss of K_2O. Clinkers B and C, for which complete data are not available, show respectively an estimated 45 and 70 per cent. solution of K_2O. The presence of K_2O and SO_3 in a molar ratio of 2·1 : 1·0, together with the fact that approximately half of the total K_2O dissolved in seven minutes, indicates the possibility that about half of the K_2O content of these clinkers may be present as K_2SO_4. Such an assumption is made and the data are considered on this basis.

One might therefore expect that the K_2O and the SO_3 would be present in solution in a molar ratio of 1 : 1. Since the amounts of SO_3 in solution were less than those required for the K_2O, and in most instances practically nil, a possible reaction involving this constituent must be considered. It has been established [3 to 8] that a nearly insoluble sulphoaluminate of calcium is precipitated from solutions containing aluminates, $CaSO_4$, and $Ca(OH)_2$. The compositions of such solutions after reaction approximate to the compositions of solutions originating from the action of water on alkali-free cements. From these observations and other considerations it is generally believed that tricalcium sulphoaluminate is formed in cement pastes. It has also been shown[8] that the presence of alkali sulphates in suspensions of clinker and water results in the formation of this double salt. The disappearance of the SO_3 from solutions in this investigation is attributed to the formation of the sulphoaluminate according to the reaction*

$$3\ CaO.Al_2O_3 + 3\ K_2SO_4 + 3\ Ca(OH)_2 + 31H_2O = 3\ CaO.Al_2O_3.3\ CaSO_4\ 31H_2O + 6\ KOH.$$

The $Ca(OH)_2$ originates from $3CaO.SiO_2$ by hydrolysis, and from solution of any free lime in the clinker. The assumption that this reaction is operative is supported by a consideration of the ionic balance in the solution. As the $\overline{SO_4}$ disappears from solution in the interval between seven minutes and two hours the $\overline{OH}$ concentration increases. This increase in the $\overline{OH}$ concentration may be balanced against the decrease in the $\overline{SO_4}$ concentration as indicated in Table 3. To illustrate the changes in the concentrations of the various ions the data for solutions from clinker No. 4 are given in Table 3.

TABLE 3.—CONCENTRATIONS IN EQUIVALENTS PER LITRE

	$\frac{1}{2}Ca^{++}$	K^+	Na^+	OH^-	$\frac{1}{2}SO_4^{--}$
7 minutes	0·08	0·396	0·015	0·213	0·197
2 hours	0·007	0·419	0·026	0·358	0·084
Change	−0·001	+0·023	+0·011	+0·145	−0·113

* The formula for the trisulphate form of the sulphoaluminate is inserted in this equation according to most views. Recently, evidence[9] has been advanced indicating that the monosulphate form of the salt is formed in cement pastes.

The observed increase in $\overline{OH}$ concentration is 0·145 equiv./1 and the observed decrease in $\overline{SO_4}$ is 0·113 equiv./1. There remains an excess of 0·032 equiv. of OH to be accounted for. The precipitation of 0·001 equivalent of Ca^{++} as $Ca(OH)_2$ resulting from supersaturation with respect to the latter caused a loss of 0·001 equivalent of $\overline{OH}$. A simultaneous hydrolysis of the compounds of K_2O and Na_2O could readily account for the remainder of OH in this summation, since the appearance of Na^+ and K^+ in the solution would be accompanied by equal equivalents of $\overline{OH}$. In the cited case the K^+ and Na^+ together total 0·034 equiv./1 which is the amount, within the limits of experimental error, required for a balance under the assumed conditions. A similar balance holds for the solutions from clinkers Nos. 5 and 6. For the remainder of the solutions the $\overline{SO_4}$ content was so low at seven minutes that the changes in the interval between seven minutes and two hours were within experimental error. The data from these solutions do not invalidate the deductions drawn for the solutions enumerated above, since the virtual disappearance of SO_4 from solution may have occurred during the first seven minutes.

Calculations based on the assumption that K_2O was dissolved as the sulphate in seven minutes (or less) from clinkers containing readily soluble K_2O are presented in Table 2. In column 2 of this table are given the molecules of K_2O per litre solution ; and in column 3 are given the molecules SO_3 which would be found per litre of solution if all SO_3 in the clinker dissolved and none precipitated. The agreement between molecules of K_2O and SO_3 is considered excellent for eight of the ten clinkers listed because, first, the K_2O found in solution may, in part, originate from other compounds than K_2SO_4 and, secondly, small absolute errors in the determinations of SO_3 in the clinkers would alter markedly the molecules of SO_3 reported in the table. Clinkers Nos. 7 and 8 are the only slag clinkers included in this study, and because of their large molecular excess of SO_3 over the K_2O (see *Fig.* 1) they cannot show this agreement. It is interesting to note that these two clinkers give the highest percentage of total Na_2O in solution and also contain sulphite and thiosulphate. Total alkalis were reported for solutions from clinkers B and C, and it was assumed that 20 per cent. (a representative amount) of the total Na_2O dissolved. Although the molecules of K_2O reported might be altered somewhat if the true amounts of Na_2O were known, the results as calculated definitely approximate a close relationship between the K_2O and SO_3.

This correlation between molecules of K_2O and SO_3 for the greater number of the clinkers containing readily soluble K_2O supports the assumption that K_2O in the clinker is combined partly as K_2SO_4 and as such is readily soluble.

In an attempt to determine directly the presence or absence of K_2SO_4 in clinker specimens, small pieces of clinker No. 4 were selected, crushed to a fine powder, immersed in a liquid of suitable index of refraction, and examined with the polarising microscope. The recorded optical properties of crystalline K_2SO_4 are as follows[10]: $\alpha = 1{\cdot}497$, $\beta = 1{\cdot}495$, $\gamma = 1{\cdot}494$, $2V(+) = 67$ deg. A liquid

of index 1·52 was selected because sulphates of calcium have indexes of refraction equal to, or higher than, this value. In this liquid small discrete grains were observed which had very low double refraction and indexes of refraction considerably lower than the liquid. In these properties the grains correspond with K_2SO_4. Attempts to identify this material in a liquid of the mean index of K_2SO_4 were inconclusive because of the small amount of the material. However, there is no known constituent of Portland cement clinker other than K_2SO_4 which has indexes of refraction lower than 1·52.

It is concluded that K_2O is probably combined in many clinkers partly as K_2SO_4, and as such is readily soluble.

The authors are indebted to Mr. P. H. Bates, who planned and directed this investigation, and to Mr. H. Insley, who made the petrographic examinations.

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Sugar Solubility Test for Cement.

IN response to inquiries, we give below the method of making the Merriman sugar solubility test referred to in our issue for April last.

Fifteen grammes of cement, 200-mesh sieve, are placed in a Nessler tube containing 100 c.c. of 15 per cent. cane sugar solution in distilled H_2O, the solution not being more than three days old. The tube and contents are quickly shaken by hand and placed on a wheel revolving about 60 times per minute. At the end of about 1 hour 50 minutes the mixture is poured into a filter paper and funnel and allowed to filter for 10 minutes, when the beaker containing the filtrate is removed. (Where the filtering time of 10 minutes is too short to produce 30 c.c. of filtrate it may be lengthened at the expense of the shaking time, but the total time from the putting of the sample into the solution to the end of the filtration must be exactly 2 hours.) Next 25 c.c. of filtrate are titrated with N_2HCl in the presence of phenolphthalein, and the number of cubic centimetres of acid to the end point is the first measure of sugar solubility. At this stage of the test, in the case of well-burnt cement which has been kept dry, the solution will be practically clear and only traces of Fe_2O_3 and Al_2O_3 will be in suspension. In the case of under-burnt cement, or cement which has been exposed to moisture, the solution will be heavily clouded and the end point must be approached slowly. The titration is then continued until the solution is crystal clear and

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nothing remains in suspension. The total number of cubic centimetres of acid from the beginning to the final clear point is the second measure of the sugar solubility.

The test is to be made at room temperature. It is supposed to disclose the quality of the cement and to indicate the character of the hydration products which will be released in the completed concrete. The specification for Portland cement of the New York Board of Water Supply places limits of 8 c.c. for the phenolphthalein end point and 10 c.c. for the final clear point.

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Heats of Hydration of Portland Cements.

ACCORDING to the *Technical News Bulletin* of the United States National Bureau of Standards, a precision calorimeter costing several thousand dollars was used by the Bureau to measure the heat of hydration of cements used in the construction of Boulder Dam. This was measured by subtracting the heat of solution of the hydrated cement from that of the unhydrated cement. More than 5,000 determinations of the heat of solution of the cements used in the Boulder Dam were made with this apparatus. More recently a simpler apparatus, consisting essentially of a jacketed vacuum flask, a Beckmann thermometer and a motor-driven stirrer (the total cost of which is less than one hundred dollars) has come into use among cement testing laboratories.

This apparatus has been made part of certain Federal specifications. A study of the reproducibility of results obtained with the vacuum-bottle calorimeter was recently completed, twelve determinations of heat of hydration having been made on each of five different cements. It was found that in half of the cases the difference between any two determinations of the heat of hydration of the same cement did not exceed one calorie per gramme. As a larger number of cases is included, the maximum differences increase. In 66 per cent. of the cases the maximum difference did not exceed 1·5 calories, and in 95 per cent. of the cases the maximum difference was less than 2·9 calories per gramme. This degree of reproducibility compares favourably with that of the physical methods used in cement testing.

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